

GEORGIA INSTITUTE OF TECHNOLOGY

OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT TERMINATION

Date: November 23, 1970

Project Title: Magnetic Rotation Spectra of Simple Molecules

Project No: B-1533

Principal Investigator: Dr. W. H. Eberhardt

Sponsor: National Science Foundation

Effective Termination Date: November 15, 1970

Clearance of Accounting Charges: All acceptable charges have cleared; the final  
fiscal report has been submitted.

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## FIRST ANNUAL TECHNICAL REPORT

NSF Grant GP-2408

to

Georgia Institute of Technology

Atlanta, Georgia, 30332

W. H. Eberhardt, Principal Investigator

Magnetic Rotation Spectra of Simple Molecules

March 1, 1965

JAN 5 1965

Preface

This Grant, GP-2408, has provided continuity in our program of study of magnetic rotation spectra initiated several years ago and supported since October 1961 by funds from the National Science Foundation.

Progress achieved during the earlier grant, G-19512, was reported in our Second Annual Technical Report and Final Report for that Grant, dated August 15, 1964. Our general plans have also been outlined in that Report.

General Summary

Progress since the last report, August 15, 1964, has been regrettably and disappointingly slow, partially because of limitations in personnel and facilities, partially because of the complexity of the problems being studied.

Studies on stable species, especially  $\text{SO}_2$ , have continued through the work of Dr. Brinkley Snowden. Some success has been achieved in the

analysis of the exceedingly complex spectra found earlier, especially in the rotational structure of some of the bands in the 2900A region, but the general problem is still far from completed. Dr. Snowden has also found a MRS in pyrazine at a location previously thought to be associated with the singlet-triplet absorption, and hence, we have been able to confirm that assignment. The fine structure of the observed bands is most interesting and resembles that of  $\text{CSCl}_2$  in exhibiting only one very sharp and concentrated feature near what we believe to be the band origin. We believe, but have not yet proved, that this feature arises from the single excited state level,  $K' = 0$ , in a symmetric rotor description and that this type of spectrum is characteristic of oblate symmetric rotors in which the spin is coupled to an axis in the molecule perpendicular to the axis of rotational symmetry.

Both the pyrazine and  $\text{SO}_2$  spectra require higher resolution than obtainable with our previous instrumentation to clarify many significant questions, such as the demonstration of the single excited state K value. A new grating and mounting have been obtained from funds provided by this Grant and considerable effort has been devoted to their proper installation and to the design and construction of an order-sorter to permit use of the grating in very high orders where both its blaze and resolution should be optimum. To date, the performance of this grating has been very disappointing in spite of the strenuous efforts to accommodate it properly in the spectrograph.

The studies on IBr are still incomplete due largely to the lack of manpower. Mr. Sullivan, who was the prime investigator in this problem,

completed his association with our group in August and has subsequently been in Zurich, Switzerland. It is hoped that this problem can be completed this coming summer.

The pulsed experiments, which represented the new phase of the proposal, are proceeding slowly due largely to the difficulty in obtaining and constructing the equipment. Only recently has the room in which these experiments are to be done been properly air-conditioned and, due to a collection of tragi-comic circumstances, acquisition of electronic components was delayed for a period of several months. At present, most of the equipment is on hand; two power supplies, one of 8000, the other 15,000 volts are completed; a delay circuit has been constructed; the capacitors have been acquired; and current efforts are devoted to assembling the entire facility.

The basic program for this work is the following:

1. A detailed study of magnetic rotation of a single absorption line: we hope to sweep the components of a neon emission line by means of a pulsed Zeeman magnet across individual lines in the MRS spectrum of ICl and thereby do exactly the experiment the theory is set up to describe. This experiment will involve a pulsed Zeeman magnet, and a steady or pulsed magnetic field around the sample.
2. A study of the dependence of the intensity of the MRS of a stable species on the magnetic field strength. In this experiment, a steady source will be used, and the magnetic field around the sample will be pulsed. We anticipate an effect in which the

intensity of the MRS increases with field to a maximum, then decreases. The field at the maximum should be relatable to the spin-rotational coupling constants.

3. Conventional photoflash experiments will be examined in an effort to get experience with the generation of radicals and their study with short-duration flashes. This experiment will involve two pulsed systems: the photolysis flash and subsequently, a spectroscopic source flash. There is nothing novel about this experiment except its unfamiliarity to us.
4. MRS of flash-generated species will then be studied by a sequence of pulsed discharges: First, perhaps, a pulse will be started to generate the magnetic field. At an appropriate time before the field attains its maximum value, the photoflash discharge will occur, followed after a predetermined interval by a source flash at a time when the magnetic field and the concentration of radicals are both maximum. Obviously, this experiment will be very tricky, and it appears late in our hopeful program for that reason.

We expect to be able to test the feasibility of the experiment outline under (1) above within the next few weeks.

### Personnel

1. During the tenure of the present grant, GP-2408, one recent graduate, Wayne Sullivan, who has been associated with the work for the past two years, worked on the program for a period of two months after his graduation and before leaving for Zurich.

2. Dr. Brinkley Snowden, Ph.D. Vanderbilt, 1963, has devoted full-time to the program.
3. Mr. Arnold Stalder, who has this fall completed all requirements for his Ph.D. degree except for his thesis research is now devoting full time to the program. He is now on a NASA Fellowship.
4. The Principal Investigator devoted two months to this program during the summer of 1964 and is spending about 30% of his effort on the program during the academic year.

#### Financial Support and Rate of Expenditure of NSF Funds

Because of the unavailability of suitably prepared graduate students, funds budgeted in the Grant for graduate research assistants have not been spent. Furthermore, an in-house NASA grant has contributed heavily to the support of the pulsed experiments and provided for one-month summer salary of the Principal Investigator, W. H. Eberhardt. The Grant GP-2408 provided one other month summer stipend for W. H. Eberhardt. The NASA grant also provided short-term support for an electronics technician who is now full-time on the staff of the School of Chemistry.

Following approval by Dr. Robert Linnell of the staff of the Chemistry Division of the National Science Foundation, funds budgeted for an electronic technician were combined with those for capital outlay for the purchase of the new grating for the spectrograph. A sum of the order of \$6000 has been obtained through the NASA Grant for construction of the photoflash and pulsed system including a high-quality Tektronix oscilloscope, the capacitor bank, and other components.

Communications

No publications have resulted from this program during the period of the Grant. However, W. H. Eberhardt attended the Conference on Molecular Spectroscopy in New Hampshire during September and presented some aspects of this work at that meeting.

It is hoped that the work on IBr, SO<sub>2</sub>, and pyrazine can be completed and published before the end of the summer.

B-1533

SECOND ANNUAL TECHNICAL REPORT

NSF Grant GP-2408

to

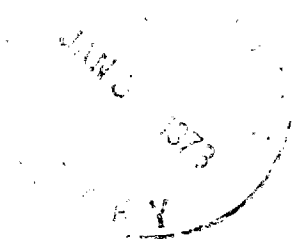
Georgia Institute of Technology

Atlanta, Georgia, 30332

W. H. Eberhardt, Principal Investigator

Magnetic Rotation Spectra of Simple Molecules

April 1, 1966



Preface

This Grant, GP-2408, continues to provide basic support for our study of magnetic rotation spectra supported since 1961 with funds from the National Science Foundation under Grant G-19512. Progress under the previous grant was summarized in our Second Annual Technical Report and Final Report of that Grant, dated August 15, 1964, which also contained general plans for future research. The basic program and progress to March 1, 1965, was summarized in the First Annual Technical Report for the NSF Grant GP-2408.

As indicated in the previous report, the general lack of enthusiasm for this type of study among the graduate students at Georgia Tech has greatly limited activity and has resulted in a much slower rate of expenditure of funds than budgeted. Consequently, a no-cost extension of the date of this grant to December 31, 1967 has been requested and granted.



### General Summary

Attempts to work at the high resolution presumably possible with the Harrison grating purchased with funds from this Grant lead us to the belief that a serious error existed in the design of the Jarrell-Ash 3.4 meter Ebert Spectrograph in that the plate holder was not in the same plane as the entrance slit. The instrument was modified to correct this defect and excellent spectra have been obtained subsequently.

These spectra have included MRS on pyrazine by Dr. Brinkley S. Snowden which have been summarized in the attached publication in the Journal of Molecular Spectroscopy. The work was also presented at the Symposium on Molecular Spectroscopy in Columbus, Ohio, June 1965.

Further studies have been made on IBr during a short period in which Mr. Wayne Sullivan spent in our laboratory before returning to Oxford, England, for graduate work. These studies remain nearly complete, but have not yet been prepared for publication.

Extensive new studies have been made on ICl in part by Dr. W. G. Trawick of the Georgia State College who worked in our laboratories during the summer of 1965 on a National Science Foundation program for science faculty. Considerable progress has been made in unraveling the complicated spectrum of this species near dissociation, but this work is not yet complete. Also, high resolution spectra in the region around  $v'=13 \leftarrow v''=1$  have made possible more significant understanding of the nature of the phenomenon and caused a re-orientation of much of our thinking in the general interpretation of the spectral information.

Although considerable effort has been spent in attempting to unravel the SO<sub>2</sub> spectrum, little progress can be reported.

The pulsed experiments, which represented the new phase of the proposal for this grant, have made good progress through the efforts of Mr. Arnold Stalder, the only graduate student now working in this area. The basic program associated with these studies was outlined in the First Annual Report of GP-2408 and has been followed. The Zeeman-swept experiment was performed with limited success due largely to the quenching of the source by the pulsing field, an unanticipated effect which we were unable to overcome completely, and due to the finite line width of the Zeeman components of the neon emission, which we had feared might prove a limiting factor. The quenching of the light source prevented sufficient stability to attempt de-convoluting techniques and we were obliged to be satisfied with observed spectra. Both circularly polarized absorption and magnetic rotation spectra were observed for single R and P branch lines with this technique and are consistent with other experience obtained through the high-resolution studies with the d.c. magnet. Some field-strength experiments have been undertaken, but it is clear that we must couple this source-system with the high-resolution instrument in order to achieve useful results. This problem is now under attack and turns out to be more complex than anticipated since we are severely intensity-limited. Although the electronic components are essentially operable for photoflash experiments, no experiments of this type have yet been performed.

Personnel supported by this Grant

1. Dr. Brinkley Snowden completed his two-year post-doctoral tenure under this grant and is now with Socony Mobil Oil Company in Dallas, Texas.

2. Mr. Wayne Sullivan spent six weeks on this program during the summer between his year at Zurich and the start of his doctoral program at Oxford.
3. Mr. Arnold Stalder has been devoting full-time to this program which constitutes the thesis research for his Ph.D. His stipend has been derived from an institutional NASA Grant.
4. The Principal Investigator devoted two months during the summer of 1965 to this program and approximately 50% of his effort during the academic year. One month of summer salary was provided through this Grant; the other month through the NASA grant.

#### Communications

1. Publications:

"Magnetic Rotation Spectrum of Singlet-Triplet Transitions,  
Part II. Pyrazine" B. S. Snowden and W. H. Eberhardt  
Journal of Molecular Spectroscopy, 18, 372 (1965)

2. Talks.

Symposium on Molecular Spectroscopy, Columbus, Ohio, June  
1965 "The Magnetic Rotation Spectrum of Pyrazine"

- b. American Physical Society Meeting, Durham, N. C. Division of  
Chemical Physics Invited Paper, Bull. Am. Phys. Soc. II, 11,  
2, 230, March 29, 1966. "Magnetic Rotation Spectra"

#### Future Plans

1. The pulsed studies will continue essentially as programmed with special emphasis on field-strength effects in  $\text{ICl}$ ,  $\text{CSCl}_2$ , glyoxal, and pyrazine.

2. High-resolution studies will be continued both with  $\text{ICl}$  in an effort to increase our understanding of the basic phenomenon and with other systems, most notably  $\text{CSCl}_2$ , and glyoxal, in an effort to understand the nature of spin-molecular coupling in these systems.
3. As of July 1, 1966, Dr. Hiram Levy, Ph.D. Harvard, 1966, will join our program in the anticipation of understanding the significance of the large amount of data now available.
4. Dr. W. G. Trawick will probably return this summer to work with us in an attempt to complete the studies near dissociation of  $\text{ICl}$ .
5. We hope that sufficient concentration of effort may be obtained to complete and publish the extensive data we have on  $\text{IBr}$ ,  $\text{SO}_2$ , and  $\text{CSCl}_2$ . All of these problems remain in a state of near completion, but are not, in our estimate, sufficiently definitive to justify publication in their present state.

B-1533

THIRD ANNUAL TECHNICAL REPORT

NSF Grant GP-2408

to

Georgia Institute of Technology

Atlanta, Georgia 30332

W. H. Eberhardt, Principal Investigator

Magnetic Rotation Spectra of Simple Molecules

December 31, 1967

NOV 1967

Preface

This Grant provides basic support for our study of magnetic rotation spectra supported since 1961 with funds from the National Science Foundation. During the period of this report, support has also been obtained from a general grant to the Georgia Institute by the National Aeronautics and Space Administration under grant number NsG-657 which provided most of the capital equipment and some salaries for the pulsed studies. Support from this source has now been exhausted.

As indicated in the two previous technical reports, the general lack of enthusiasm for this type of study among the graduate students at Georgia Tech has resulted in a much slower rate of expenditure of funds than budgeted. Only one graduate student, Mr. Arnold Stalder, worked continuously on this program and completed his doctoral work with studies on ICl. Attempts to attract qualified post-doctoral fellows have failed. Attempts to use students from other areas, notably physics, for short

periods have been of limited success only. Attempts to involve faculty members at other institutions have also been of very limited success. In each case, we feel the program has been of value to the individual concerned, but his contribution to the program has been minimal. Thus, a general reorientation of our efforts seems indicated. It is our hope that several of our unfinished problems can be completed in the next 18 month period for which a grant-extension is being requested and the work will then be terminated or given a new direction.

#### General Summary of Technical Achievements

The pulsed studies, which formed the basis for the new work proposed for this Grant, have been summarized in the First and Second Annual Reports. Equipment for these studies was developed by Stalder and extensive efforts were devoted to a study of the stable species,  $\text{ICl}$ . In spite of heroic efforts, no major novel or useful result was obtained from these studies and it seems apparent that a major improvement, of at least three orders of magnitude, in the intensity of the source is required before the experiment as originally proposed is feasible. Although Zeeman effects were observed in absorption with pulsed fields and a pulsed Lyman source, no really new information was obtained. These experiments have been discontinued.

A study which we believe is of classic significance to the interpretation of magnetic rotation spectra has been completed using a continuous source with phase sensitive detection. This work constituted part of Stalder's thesis and has been published in the Journal of Chemical Physics.

In connection with this study and also that on IBr an interesting application of the use of isotope shifts to determine the adequacy of the JWKB approximation has been found. This report was published in the Journal of Molecular Spectroscopy; copies are attached.

The study of magnetic rotation near single lines of ICl indicated the importance of magnetic mixing of neighboring J-states and may provide an important clue to resolving many of our other problems. In part to test these notions we have started a study of the CN system at 3883A which is well known as a  $^2\Sigma - ^2\Sigma$  transition. We have developed a theory which predicts the variation of intensity of the MRS with rotational quantum number N. We are now attempting to test this theory. If these experiments prove successful, we believe the theory can be extended to polyatomic systems for which the  $^2\Sigma$  and  $^3\Sigma$  diatomic models are most appropriate.

Additional effort has been devoted to IBr in an effort to test a new hypothesis for the interpretation of these data. Although the analysis of the spectrum is essentially complete, the interpretation of the results is not. Our present conjecture is that we observe in MRS only those states which correspond to "orbiting" in a diatomic collision process. If this conjecture can be substantiated, it will have major significance in the interpretation of complex diatomic spectra in which several repulsive states cross an attractive state and may actually have some significance in chemical reaction theory. Several critical arguments, both theoretical and experimental, remain to be tested before the conjecture can be exposed to criticism.

Additional efforts have been made to interpret the MRS of  $\text{SO}_2$ .

Although a start was made on this problem, with some indication of success, by a graduate student in physics during the summer of 1966, no real progress has been made. We are starting a companion study of  $S_2O$  in the anticipation that comparison of these two spectra will be interesting and significant in the interpretation of both.

#### Personnel Supported by this Grant

1. Mr. Arnold Stalder received his Ph.D. in June 1967 for work performed with the aid of this Grant. A large fraction of the capital equipment for the pulsed studies and his stipend was derived from the NASA Grant referred to in the Preface to this Report.
2. Dr. W. G. Trawick of the Georgia State College worked in this program but was supported from other sources during the summers of 1966 and 1967.
3. Mr. Douglas Wrege of the School of Physics was supported from this Grant during the summer of 1966. His work on  $SO_2$  showed promise, but he did not continue it.
4. Mr. Gerald McGowan, a graduate student in chemistry, was supported during his first year at Georgia Tech with funds from this Grant. Unfortunately, although his research on CN showed promise, his academic performance was so poor he is no longer in graduate school.
5. The Principal Investigator devoted two months during the summer of 1966 to this program and approximately 50% of his time during the fall quarter of 1966. From January 1 through



July 31, 1967, he served as Executive Director of the Advisory Council on College Chemistry in Palo Alto, California. Since August 20, he has devoted approximately 50% of his time to this program with no direct charge against the Grant.

### Communications

#### 1. Publications:

"Magnetically Induced Circular Dichroism and Birefringence in Single Lines of the Electronic Spectrum of ICl," Arnold F. Stalder and W. H. Eberhardt, Journal of Chemical Physics, 47, 1445 (1967).

"Diatomic Isotope Effects and Second-Order Corrections in the JWKB Approximation," W. H. Eberhardt, Journal of Molecular Spectroscopy, 24, 154 (1967).

#### 2. Lectures

University of Washington, July 25-August 5, 1966:

"Magneto-Optics and some Related Topics," 8 lectures.

### Future Plans

1. Tests of the conjectures on IBr will continue and we hope will lead to an interesting interpretation of these data.
2. Tests of the theory developed for CN are in process.
3. A study of S<sub>2</sub>O is in process by a second-year graduate student, Mr. Warren Twiggs, who joined this program in October, 1967.
4. Studies on ICl near dissociation should be continued by Dr.

W. G. Trawick, but most likely, little will be accomplished before summer.

5. Study of the vibrational-electronic interaction problems posed by  $\text{SO}_2$  and  $\text{CSCl}_2$  will be continued, probably by Mr. John Hardwick, also a second-year graduate student who has just joined this program.

#### Implementation

The effective date of this Grant, GP-2408, was extended to December 31, 1967. We now request continuation of this Grant on a no-cost extension through October 31, 1969. We hope by that time either to conclude our efforts in this area or to submit a new proposal if developments within that period warrant further efforts.

Fourth Technical Report

NSF Grant GP-2408

to

Georgia Institute of Technology

Atlanta, Georgia 30332

W. H. Eberhardt, Principal Investigator

Magnetic Rotation Spectra of Simple Molecules

August 31, 1969

Preface

This Grant provides basic support for our study of magnetic rotation spectra, supported since 1961 with funds from the National Science Foundation. In our previous report, dated December 31, 1967, we indicated our intention to attempt to bring this research program to a close and hoped to accomplish a reasonable termination by October 31, 1969. Although we will not be able to meet that deadline, we anticipate a change in direction of our spectral studies when the students presently involved have completed their work. Unfortunately, their progress has been much slower than desirable and I am obliged to request no-cost continuation of at least a part of this grant to provide necessary supplies and equipment for their work.

## General Summary of Technical Achievements

1. A great amount of effort has been devoted to further studies on IBr. The interpretation which seemed to be indicated earlier proved unsupportable and another has been advanced and seems firmly established. In essence, an intersystem crossing from a bound  $0^+$  state to an unbound  $^3\Pi_{0^+}$  state is avoided for a very limited number of excited state rotational and vibrational levels. Our explanation centers on the mixing of the bound and unbound states by terms in the Hamiltonian generally ignored in the Born-Oppenheimer approximation. For certain rotational and vibrational states, we believe the matrix elements of these terms between the two states may vanish and it is just those lines we observe in MRS. The consequences of this suggestion seem important to the notion of adiabatic processes and the existence of potential functions and also shed light on the nature and failure of the Born-Oppenheimer approximation. This work is nearly ready for publication; a preprint will be forwarded in the immediate future.

2. Our previous report indicated a start on the study of the MRS of CN around  $3883 \text{ \AA}^0$ . Preliminary results lead to a suggested explanation which would have considerable importance to the interpretation of all  $^2\Sigma^- \rightarrow ^2\Sigma^-$  type transitions and hence serve as a model for molecular fragments. This test required a determination of the dependence of the intensity of the MRS on the case (b) quantum number N and on magnetic field strength. This test has now been made by Mr. S. W. Twiggs and the results do not support our previous theory. New theoretical approaches are being attempted by Mr. Twiggs to search for a better insight into this problem.

3. Efforts to unravel the rotational and vibrational structure of the near ultraviolet spectrum of  $\text{SO}_2$  continue. Previous studies on the problem by Dr. Brinkley Snowden demonstrated the existence of a MRS for the triplet system, as anticipated, but the historically well-known MRS of the strong system responsible for absorption around  $3000\text{\AA}$  has resisted analysis. We believe the MRS holds an important clue in this case and provides rotational data deserving analysis. The problem has been approached in three ways:

1. A direct study of the MRS of  $\text{SO}_2$  based on combination relations using the very well-characterized ground-state rotational energies.

2. A companion study of the isotopically enriched species,  $\text{SO}_2^{18}$ , which has been prepared and is now under way.

3. A related study on the MRS of  $\text{S}_2\text{O}$ .

Studies on  $\text{SO}_2$  are being carried out by Mr. John Hardwick. Mr. S. W. Twiggs has devised a technique for the preparation of  $\text{S}_2\text{O}$  and monitored the concentration by absorption spectra, but the MRS has not yet been observed.

### Student Support

During the period of this report, the following students have been supported in part or in full by funds from this grant:

- Mr. John Hardwick, a graduate student who entered Georgia Tech graduate school Fall, 1966, was supported as a graduate research assistant from July 1, 1968, to the present.
- Mr. Warren Twiggs, a graduate student who entered Georgia Tech graduate school Fall, 1966, and has been supported on NASA Traineeship. This grant provided research support.
- Mr. Daniel McLemore, an undergraduate who worked without compensation in this program during the Winter and Spring Quarters of 1968 and who was supported for full-time work during the summer of 1968.
- Mr. John Vaitkunas, a graduate student who entered Georgia Tech graduate school Spring, 1969, and is supported for study and research this summer.

Mr. McLemore assisted us in the development of microwave cavities for excitation of atomic spectra for calibration of our spectrograph and devoted a large effort to the search for emission from IBr excited by a variety of electrical techniques: microwave discharge, radio-frequency discharge, and 60-hertz high-voltage discharge. Unfortunately, no spectra were obtained better than those already published and our original plan of carrying through a rotational analyses of bands reported by Verma and Venkateswarlu proved impracticable.

Mr. Vaitkunas is currently looking for fluorescence from IBr excited by white light. We propose that short runs of  $v'$  and  $J'$  may appear in fluorescence corresponding to the lines which our magnetic rotation studies show as sharp.

### Other Changes in Personnel

As of July 1, 1969, Dr. W. H. Eberhardt, the Principal Investigator, was to become Associate Dean of the General College on a half-time basis; the other half time was to be devoted to this research, as it has been for some time past. As a consequence of other changes within the administration, Dr. Eberhardt served in that capacity only one month. Effective August 1, 1969, he became Acting Dean, a rather more demanding position, with a consequent reduction in time and energy to 20% within the School of Chemistry, still totally devoted to this research. This situation is likely to persist through the present academic year.

### Communications

No publications have resulted from this work during the period covered by this report. The work on IBr should be submitted soon.

An invitation to participate in the Faraday Society Discussion on Magneto-Optics, scheduled for December 1969, was declined due to the demands of the Dean's position. Our reputation as a source of unpublished data seems to persist.

## FINAL TECHNICAL REPORT

NSF Grant GP-2408

to

Georgia Institute of Technology

Atlanta, Georgia 30332

W. H. Eberhardt, Principal Investigator

Magnetic Rotation Spectra of Simple Molecules

November 10, 1970

Preface

Our original proposal of February 9, 1961, laid out a five-year program of studies on Magnetic Rotation Spectra of Simple Polyatomic Molecules. The NSF grant, G-19512, activated in October 1961 provided major instrumentation and support of personnel for a two-year period which permitted us to follow that proposal closely. The grant GP-2408 was based on a proposal to continue these studies and institute a new program using a pulsed field to study photoflash-generated species. Additional support for capital equipment and personnel for the pulsed studies was obtained from a general grant to the Georgia Institute of Technology by the National Aeronautics and Space Administration and permitted us to stretch National Science Foundation funds farther than originally budgeted.

Summary of Achievements

During the period of these two grants we have accomplished the following:



1. Completed and published what we consider to be a classic study of magnetically induced circular dichroism and birefringence in single lines of an electronic spectrum. The system studied was the  ${}^3\Pi_1 \leftarrow {}^1\Sigma$  system of ICl. The work constituted part of the PhD thesis of Arnold F. Stalder submitted in January 1967.

2. Completed a similar study on the  ${}^1\Sigma \leftarrow {}^1\Sigma$  system in CN which was intended to serve as a model for extending the technique and theory to polyatomic radicals. This study is part of the PhD research of Mr. S. W. Twiggs. The CN system turned out to be more complex than anticipated because of perturbations by the  ${}^2\Pi$  state. Other systems are now being sought to pursue this objective.

3. Discovered and extended previous studies of the magnetic rotation spectra corresponding to singlet-triplet transitions in several molecules, notably,  $\text{SO}_2$ ,  $\text{CSCl}_2$ , pyrazine and glyoxal. The studies on pyrazine were interpreted according to the vector model based on a case (b) coupling scheme and published in 1965. Studies on  $\text{SO}_2$  and  $\text{CSCl}_2$  were presented at the Molecular Spectroscopy Symposium of June 1964 and the American Physical Society meeting of March 1966, respectively, but are otherwise unpublished.

4. Completed the rotational-vibrational analysis of the MRS of the  $0^+ \leftarrow {}^1\Sigma$  transition in IBr discovered by us earlier. Although analysis of the spectrum is complete, interpretation of its origin remains obscure and the work has not yet been published.

5. Developed Gaussian-orbital techniques for the study of bonding and the treatment of magnetic coupling phenomena in simple molecules. This study constituted the PhD thesis of Jerry L. Whitten in 1963 and has had significant impact on subsequent *a priori* calculations made by him and others. The original purpose of the study was to evaluate by *a priori*

calculations the energy states including spin-orbit interactions in glyoxal in the hope that these calculations would permit us to unravel the MRS. The calculations were successful but did not help significantly in our understanding of the spectrum.

6. Extended the JWKB treatment to evaluate second-order correction terms by measurements of isotopic shifts in diatomic molecules and tested this technique with data on ICl. This work was published in 1967. The problem was undertaken to clarify interpretations of isotope effects in IBr and the results contributed substantially to our success in analyzing the MRS of IBr.

7. Designed and constructed an order-sorter of novel design to be used in conjunction with the high-order grating in the Jarrell-Ash Ebert spectrograph. Descriptions of this device and its performance will be published.

#### Other Programs and Contributions

The pulsed studies were pursued vigorously by A. F. Stalder but ultimately proved impracticable. A technique using a Zeeman-swept neon emission line was developed to scan single lines in the MRS of ICl. This technique was interesting but the results contributed little to our understanding and was replaced by conventional high resolution, photoelectric scanning. High-field studies based on pulsed magnetic fields and pulsed sources were also pursued but led to no new understanding.

A variety of techniques was used to search for fluorescence of IBr by an undergraduate, Mr. Dan McClemore, and a short-time graduate student, Mr. John Vaitkunas. No fluorescence was found.

Studies on  $\text{SO}_2$  and  $\text{SO}_2$  enriched with  $\text{O}^{18}$  have been carried out by Dr. Brinkley Snowden and Mr. John Hardwick. Isotope shifts of the bands around  $3000 \text{ \AA}$  have been determined approximately but more accurate values must be obtained from rotational analysis of these bands. A computer-based technique for scanning plates and reduction of the data has been developed recently by Mr. Hardwick. This technique should improve the accuracy of our data by an order of magnitude and should permit rotational analysis of the  $\text{SO}_2$  bands by combination-relation methods.

Preliminary studies on  $\text{S}_2\text{O}$  have been made by S. W. Twiggs; no MRS has yet been observed for this molecule.

The grant provided some developmental funds and publication costs of a paper on "Two-Lecture Experiments in Elementary Thermodynamics" presented at the symposium on the teaching of thermodynamics at the American Chemical Society meeting of September 1969.

### Personnel

In addition to the principal investigator, the following individuals or their research have been supported by the grant during the period October 1963 through June 1970.

1. Wayne Sullivan, summers 1962, 63, 64, 65. Dr. Sullivan graduated from Georgia Tech with a B.S. degree in Chemistry in 1964, spent the year 1964-65 in the Eidgenoschene Technische Hochschule in Zurich, and studied for and received the D.Phil. degree with Professor Coulson at Oxford University in 1968. He is now Assistant Professor of Mathematics at Georgia Tech.

2. Arnold F. Stalder, 1963-67, was supported in part by funds from the NASA grant to Georgia Tech and in part by funds from this grant. He received his PhD in 1967, spent the year 1967-68 as a postdoctoral research assistant in Chemical Engineering and is currently employed by Texas Instruments Company in Dallas, Texas.

3. Dr. Brinkley Snowden, PhD, Vanderbilt, 1963, was supported as a postdoctoral research assistant for the period 1963-65. He has since been employed by Socony Mobile Company in Dallas, Texas.

4. Mr. John L. Hardwick, B.S., Princeton, 1966, is a graduate student in Chemistry and was supported from September 1967 to June 1970.

5. Mr. S. W. Twiggs, B.S., Georgia Tech, 1966, has been supported by a NASA traineeship but his work has been supported by this grant since September 1967.

6. Two short-time graduate students in Chemistry: Mr. Gerald McGowan, 1964 and Mr. John Vaitkunas, 1969. Neither individual is now in school. In addition, a graduate student in Physics, Mr. D. E. Wrege, was supported during the Summer of 1966. Mr. Wrege is now a candidate for the PhD in Physics at Georgia Tech.

7. Dr. W. G. Trawick, PhD, Georgia Tech, 1955, and now Head of the Department of Chemistry of Georgia State University spent the summers of 1965 and 1966 working in this program. He was supported by a NSF Science Faculty Summer Program and contributed extensively both to our program in MRS and to studies in the application of the JWKB treatment to RKR calculations of ICl and other systems.

#### Continuation of the Program

It is our intention to bring this study of magnetic rotation spectra to a close when the present students, S. W. Twiggs and J. L. Hardwick,

have completed their work. At present, the following aspects are incomplete but under study:

1. Search for significance of the results obtained for IBr; this study has been a major concern of the principal investigator, W. H. Eberhardt.

2. Continuation of theoretical studies on the  ${}^2\Sigma \leftarrow {}^2\Sigma$  system in CN and experimental studies on related systems in  $N_2^+$  and SiN; S. W. Twiggs is conducting these studies.

3. Continuation of the analysis of the MRS of  $SO_2$  and  $SO_2^{18}$ ; J. L. Hardwick has made good progress in unraveling the isotope effects and is in a position to start the rotational analysis.

4. Continuation of related studies especially those pertaining to  $S_2O$  and  $CSCl_2$ .

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#### Communications

##### a. Theses:

Arnold F. Stalder, PhD, January 1967, "Studies of Magnetic Effects of  $ICl$ ".

##### b. Publications:

1. "Magnetic Rotation Spectrum of Singlet-Triplet Transitions, Part II, Pyrazine", B. S. Snowden and W. H. Eberhardt, Journal of Molecular Spectroscopy, 18 372 (1965).

2. "Magnetically Induced Circular Dichroism and Birefringence in Single Lines of the Electronic Spectrum of  $ICl$ ", Arnold F. Stalder and W. H. Eberhardt, Journal of Chemical Physics, 47, 1445 (1967).

3. "Diatomic Isotope Effects and Second-Order Corrections in the JWKB Approximation", W. H. Eberhardt, Journal of Molecular Spectroscopy, 24 154 (1967).
4. "Two Lecture Experiments in Elementary Thermodynamics", W. H. Eberhardt, Journal of Chemical Education, 47, 362 (1970).

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